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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the Production of Manganese Solutions and the Electrowinning of Metallic Manganese therefrom

We, ELECTRIC FURNACE PRODUCTS COMPANY LIMITED, of Canada Life Building, City of Toronto, Province of Ontario, Dominion of Canada, a Corporation organised under the Acts of the Dominion of Canada, (Assignees of MICHAEL CARLOSELLA, a Citizen of the United States of America, of 517, 82nd Street, Niagara Falls, State of New York, United States of America), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for the preparation of manganese solutions substantially free of iron and other heavy metal impurities from manganese-bearing materials, and to the electrowinning therefrom of metallic manganese.

Heretofore, one practice employed was to treat a ferro-manganese alloy or manganese ore with a mineral acid and then, after filtration, remove the metallic impurities by precipitation of their sulphides to produce a solution containing manganese mineral salt suitable for chemical and electro-chemical uses. However, ferro-manganese alloys are relatively costly, and manganese ore is not readily soluble in acid unless it is first reduced to convert the manganese to the bivalent state.

It has now been found that solutions containing manganese sulphate or chloride suitable for chemical and electrochemical purposes can be obtained without a preliminary reduction step from a furnace slag containing manganese in the bivalent state together with a metal sulphide capable of yielding sulphide ions upon reaction with sulphuric or hydrochloric acids. Such slags, produced for example as by-products from the commercial process for the production of ferromanganese and steel, have hitherto been considered valueless, and the present invention now gives them practical utility as a valuable source of manganese metal.

Specifically, the present invention is directed to a process for the production of manganese sulphate or chloride solution substantially free from iron and other heavy metal impurities (e.g. copper, lead, nickel, cobalt, or zinc), which includes leaching an impure manganese-bearing material as hereinafter defined in sulphuric or hydrochloric acid to form a leach slurry, adjusting the pH value of the slurry to between 4.0 and 7.5 in the presence of sufficient sulphide ions to precipitate substantially all of the heavy metal impurities as sulphides, adding an oxidizing agent to precipitate the remainder of the iron impurity, and removing the precipitates from the solution. According to the invention, the manganese-bearing material to be employed is a furnace slag containing manganese in the bivalent state together with a metal sulphide capable of yielding sulphide ions upon reaction with the mineral acid. In the event that the manganese slag contains less than 0.01% of the heavy metal impurities other than iron, the oxidizing agent may be added directly to the leach liquor containing the sulphide precipitates, thereby eliminating a separate filtration for the removal of the sulphides.

In carrying out the present invention, the manganese-bearing material is leached with sulphuric or hydrochloric acid. To this leach slurry a suitable source of sulphide ions may then be added in a quantity sufficient to make up for any possible deficiency of sulphide ions. The additional sulphide ions may be introduced by adding, for example, hydrogen sulphide or ammonium sulphide. The pH of the leach slurry so obtained is then adjusted to approximately 4.0 to 7.5 by the addition of a base. Should it be desired to produce ammonium and manganese-containing sulphate or chloride solution then ammonia should be employed as the pH-adjusting base. Should it be desired to produce a solution of manganese sulphate or chloride alone, then calcium oxide or other suitable base should be employed to obtain the proper pH adjustment.

Bases that separate or can easily be separated from the as-formed filtrate, such as the oxides, hydroxides and carbonates of the alkaline earth metals, are considered suitable for pH adjustment when it is desired to produce a solution of manganese sulphate or chloride alone.

After the pH adjustment the resulting pulp is filtered to remove the residue which consists largely of silica, alumina, carbon, and sulphides of objectionable metal impurities, i.e., sulphides of copper, lead, nickel, cobalt and zinc. If a sufficient amount of sulphide ions is present in the solution a large part of the iron impurity will also be precipitated as ferrous sulphide. The resulting filtrate is treated with hydrogen peroxide or equivalent oxidizing agent. The iron precipitate so obtained is removed from the solution which will then consist of an aqueous manganese sulphate or chloride solution or a manganese and ammonium sulphate or chloride solution depending on the pH-adjusting base that was employed.

The foregoing method, in the case where ammonia is used as the base, resulting in manganese and ammonium containing sulphate or chloride solutions may effectively be adapted to a cyclic process for the electrowinning of metallic manganese. This is achieved by adding sulphur dioxide to the solution of manganese and ammonium salts obtained in the above manner, to form cell feed, introducing the cell feed into the cathode compartment of a diaphragm electrolytic cell, electrolyzing the cell feed to form metallic manganese at the cathode and to form in the anode compartment of the cell an anolyte, and recycling the anolyte to the leaching step hereinbefore described.

For many years manganese-bearing materials have been produced as by-products of many commercial smelting operations. An example of such a process is the commercial method for the production of ferromanganese wherein manganese ore is smelted with carbon and iron or iron ore to yield ferromanganese and manganese slag. Manganese-bearing slags have also been obtained as by-products from steel making furnace operations. The manganese-bearing materials obtained as by-products of such operations are rich in manganese and the use of these materials as a source of solution for the electrowinning of manganese would greatly reduce the complexity of the former processes by obviating the step of reducing the manganese ore and simplifying the impurity-removal processes heretofore required when manganese ore was employed as the source of such solutions.

The present invention reduces the complexity of the former cyclic processes for the electrowinning of manganese by providing a process wherein solutions suitable for the electrowinning of high purity manganese metal are prepared directly from the manganese-

bearing materials obtained from other commercial processes.

The solutions prepared by the present invention give electrolytes which will permit the maintenance of a high current efficiency in the electrowinning step and continued operation over long periods of time without the buildup of impurities in the cycle.

In the accompanying drawings:—

Fig. 1 is a flow sheet illustrating the steps of a process embodying the invention wherein manganese and ammonium sulphate solutions are produced.

Fig. 2 is a flow sheet illustrating a modified process embodying the invention when a high purity manganese-bearing slag is employed to produce manganese and ammonium sulphate solutions;

Fig. 3 is a flow sheet illustrating the steps of a process embodying the invention wherein manganese sulphate solutions are produced;

Fig. 4 is a flow sheet illustrating a modified process embodying the invention when a high-purity manganese-bearing slag is employed to produce the manganese sulphate solutions;

Fig. 5 is a flow sheet illustrating a modification of the process illustrated in Fig. 1 to produce a cyclic process for the electrowinning of metallic manganese; and.

Fig. 6 is a flow sheet illustrating a modified cyclic process for the electrowinning of metallic manganese which may be employed when a high purity manganese-bearing slag is used.

Referring to Fig. 1 of the drawings, box 1 shows the leaching step in which ammonia gas is added to adjust the pH. The filtrate is separated from the residue as is illustrated in box 2. As shown in box 3, the iron-oxidizing reaction is accomplished by the addition of an oxidizing agent. Thereupon, the iron residue is separated from the manganese and ammonium sulphate solution, as is indicated in box 4 of the flow sheet.

In Fig. 3 of the drawings box 1a shows the leaching step to which calcium oxide, or other suitable base, is added to adjust the pH. The residue is removed from the filtrate as is illustrated in box 2a. As shown in box 3a, a suitable oxidizing agent is added to oxidize the iron impurities. Thereupon, the iron residue is separated from the manganese sulphate solution, as is indicated in box 4a of the flow sheet.

In the process of the present invention, when the pH of the leach slurry is adjusted to about 4.0 to 7.5, the sulphide ions, carried into the leach slurry with the manganese-bearing material, as well as the sulphide ions introduced to make up for any deficiency in the leach slurry, react with the heavy metal impurities, such as copper, lead, nickel, cobalt and zinc to produce sulphides of these heavy metal impurities. In order to provide manganese-containing solutions substantially free from these heavy metal impurities, it is im-

perative that an amount of sulphide ions sufficient to combine with substantially all of the heavy metal impurities derived from the manganese-bearing material be present in the leaching step. If the manganese-bearing material does not have this sufficient quantity of sulphide ions initially associated with it, it will be necessary to make up for the deficiency by adding a source of sulphide ion to the leaching step prior to the pH adjustment of the leach slurry.

It has been discovered that when manganese-bearing material contains less than approximately 0.01% of objectionable heavy metal impurities, such as copper, lead, nickel, cobalt and zinc, the process of the present invention may be simplified to the extent that the filtration step prior to the oxidation step, described hereinabove in connection with Fig. 1, may be eliminated and the oxidation step may be carried out as part of the leaching step. In this case some of the heavy metal impurities may carry through to the manganese-containing solution but are of sufficiently low concentration to be permissible. This simplification of the process when higher purity manganese-bearing materials are employed is illustrated by Figs. 2 and 4 of the drawing. As there shown, a manganese slag is leached with sulphuric acid.

In Fig. 2 the pH of the leach slurry is adjusted to approximately 4.0 to 7.5 with ammonia and the resulting pulp is treated with hydrogen peroxide or other suitable oxidizing agent. This entire operation is illustrated by box 5 of the flow sheet. The pulp is then filtered, as illustrated by box 6 of the flow sheet, to remove the residue and yield an aqueous solution of manganese and ammonium sulphates.

In Fig. 4 the pH of the leach slurry is adjusted to approximately 4.0 to 7.5 with a suitable base, such as calcium oxide, and the resulting pulp is treated with hydrogen peroxide or other suitable oxidizing agent. This is illustrated in box 5a of the flow sheet. The pulp is then filtered, as illustrated in box 6a of the flow sheet, to remove the residue and yield an aqueous solution of manganese sulphate.

In both Figs. 2 and 4 of the drawings provision is made for the introductions of additional sulphide ions to the leaching step should an insufficient amount be associated with the manganese slag.

Referring to Figure 5 of the drawings, the leaching, filtering, oxidising and filtering steps illustrated by boxes 11, 12, 13 and 14 respectively are identical with those illustrated by boxes 1, 2, 3 and 4 of Fig. 1, and hereinbefore described, except in that a major portion of the sulphuric acid or hydrochloric acid used in the leaching process, is obtained from recycled anolyte, from which magnesium has been removed, if necessary, the remainder

of the leaching acid being make up acid. Sulphur dioxide is added to the filtrate from the filtration stage illustrated by box 14, and the resulting solution is introduced into the cathode compartment of a diaphragm electrolytic cell as cell feed.

The cell for the electrowinning of manganese from such solutions may employ any suitable electrodes. When sulphate solutions are used anodes of 99% lead-1% silver alloy may be employed while graphite anodes may be employed when chloride solutions are used.

Electrolysis of sulphate solutions in the cell results in the formation of high purity manganese metal at the cathode and the mineral acid and some manganese dioxide at the anode. This step is illustrated in box 15 of the flow sheet.

It has been found that very satisfactory metal is obtained at satisfactory current efficiencies when the cathode current density is in the range of approximately 160 to 860 amperes per square meter and the anode current density is in the range of approximately 320 to 1720 amperes per square meter.

When a sulphate bath is used, the anolyte obtained from the electrowinning step is cooled to a temperature less than the cell operating temperature whereupon mixed magnesium-ammonium salt crystals are formed. The cooler is shown as step 16 in the drawing. These crystals are removed from the solution whereupon the solution is recycled to the leaching step. The crystal removal step is illustrated by box 17 of the flow sheet.

In order to provide electrolyte solutions substantially free from these heavy metal impurities, it is imperative that an amount of sulphide ions sufficient to combine with substantially all of the heavy metal impurities derived from the manganese-bearing material be present in the leaching step. If a sufficient amount of sulphide ions is not present in the leach slurry all of the heavy metal impurities will not be removed from the leach slurry in the form of sulphide precipitates and would, therefore carry through the entire cycle and result in a marked drop in current efficiency in the electrowinning step.

The use of a magnesium removal step in the electrowinning process of the present invention is made necessary by the fact that, if not removed in a planned step, complex magnesium salts will not crystallize out in the first sufficiently cool part of the cycle thereby causing breakdown. The removal is therefore included where made necessary by the magnesium content of the slag employed. The entire quantity of anolyte need not be treated in the magnesium purification step, but the treatment of merely a portion of the anolyte will ordinarily suffice to keep the magnesium concentration sufficiently low to prevent such a buildup in the cycle.

When the manganese-bearing material contains less than approximately 0.01% of objectionable heavy metal impurities, such as copper lead nickel, cobalt and zinc, the cyclic process of the present invention may be simplified to the extent that the filtration step 12 prior to the oxidation step, 13 described hereinabove, may be eliminated and the oxidation step 13 may be carried out as part of the leaching step. In this case, some of the heavy metal impurities may carry through the cycle but are of sufficiently low concentration to permit satisfactory operation of the process. This simplification of the process when higher purity manganese-bearing materials are employed is illustrated in Fig. 6 of the drawings. As there shown, a manganese slag is leached with sulphuric acid the major portion of which is obtained from recycled anolyte, from which the magnesium has been removed, and the remainder from make-up acid. The pH of this leach slurry is adjusted to approximately 4.0 to 7.5 by the addition of ammonia. The resulting pulp is also treated with hydrogen peroxide or an equivalent oxidizing agent. This entire operation is indicated by box 18 of the flow sheet. The pulp is then filtered to remove the residue which consists of silica, alumina, carbon, iron precipitate, and some of the objectionable heavy metal impurities. This is shown in box 19 of the flow sheet. The filtrate so obtained is treated with sulphur dioxide to produce cell feed for the electrowinning step. The electrowinning step 20 and magnesium removal steps 21 and 22 are identical with the corresponding steps employed in Fig. 5 and discussed hereinabove.

The nature of the invention and the manner in which it is carried out are further illustrated by the following examples.

EXAMPLE I

3800 grams of ferromanganese slag (61.0% MnO, 20.0% SiO₂, 12.8% Al₂O₃, 0.90% MgO, 0.60% TiO₂, 0.2% S, 0.10% C, 0.50% Fe, 0.01% Cu, 0.006% Ni, 0.04% Co) was leached with 100 liters of sulphuric acid solution containing 30.9 grams H₂SO₄/liter. The resultant pulp was adjusted to a pH of approximately 6.65 by the addition of about 90 grams of NH₃ gas. The resultant residue was separated from the filtrate, whereupon 0.01 liters of H₂O₂ was added. The as-formed iron residue was separated from the solution to yield 100 liters of high purity manganese and ammonium sulphate solution (15.16 grams/liter Mn, 3.5 grams/liter (NH₄)₂SO₄).

EXAMPLE II

3800 grams of ferromanganese slag (60.7% MnO, 18.96% SiO₂, 13.92% Al₂O₃, 0.87% MgO, 0.63% TiO₂, 0.14% S, 0.08% C, 0.08% Fe, 0.004% Cu, 0.002% Ni, 0.001% Co) was leached with 100 liters of sulphuric acid solution containing 30.9 grams H₂SO₄/liter. The

resultant pulp was adjusted to a pH of approximately 6.7 by the addition of about 90 grams of NH₃ gas. To the pulp 0.01 liters of H₂O₂ was then added. The residue was then removed from the solution to yield 100 liters of high purity manganese and ammonium sulphate solution (15.16 grams/liter Mn, 3.5 grams/liter (NH₄)₂SO₄).

EXAMPLE III

74 grams of ferromanganese slag (61.0% MnO, 20.0% SiO₂, 12.8% Al₂O₃, 0.90% MgO, 0.60% TiO₂, 0.2% S, 0.10% C, 0.5% Fe, 0.01% Cu, 0.006% Ni, 0.04% Co) was leached with 43.5 grams of H₂SO₄. The pH of the leach slurry was then adjusted to 6.8 by the addition of lime slurry. The as-formed filtrate was separated from the residue and treated with H₂O₂ to remove the iron impurities and yield a liter of high purity manganese sulphate solution containing 22.35 grams of manganese.

EXAMPLE IV

70 grams of ferromanganese slag (60.7% MnO, 18.96% SiO₂, 13.92% Al₂O₃, 0.87% MgO, 0.63% TiO₂, 0.14% S, 0.08% C, 0.08% Fe, 0.004% Cu, 0.002% Ni, 0.001% Co) was leached with 43.5 grams of H₂SO₄ to which lime slurry was added to adjust the pH to 6.6. H₂O₂ solution was then added to separate the iron impurities. The as-formed residue was separated from the solution to yield one liter of high purity manganese sulphate solution containing 21.6 grams of manganese.

EXAMPLE V

3800 grams of ferromanganese slag (61.0% MnO, 20.0% SiO₂, 12.8% Al₂O₃, 0.90% MgO, 0.60% TiO₂, 0.2% S, 0.10% C, 0.50% Fe, 0.01% Cu, 0.006% Ni, 0.004% Co) was leached with 130 grams of make-up sulphuric acid, and 100 liters of recycled anolyte (containing 120 grams/liter Mn, 29.6 grams/liter of free H₂SO₄, and 125 grams/liter (NH₄)₂SO₄). This leach slurry was adjusted to a pH of approximately 6.65 by the addition of 90.0 grams of ammonia gas. The resulting pulp was filtered and the 10 liters of filtrate was found to contain 27.2 grams/liter Mn, 128.5 grams/liter (NH₄)₂SO₄, and some iron, magnesium and sulphide ions. To this filtrate was added, as an oxidation step, .01 liter of 36% hydrogen peroxide solution. The as-formed solution was agitated for 30 minutes at room temperature whereupon a precipitate was formed. This precipitate was removed from the filtrate and was found to contain 3.0 grams Fe and traces of heavy metal impurities. Sulphur dioxide gas was then added to the filtrate to obtain 100 liters of cell feed having the composition 27.16 grams/liter Mn, 128.5 grams/liter (NH₄)₂SO₄, and 0.68 grams/liter SO₂.

This cell feed solution was introduced into the cathode compartment of a diaphragm electrolytic cell, having anodes and cathodes as described hereinabove, and electrolyzed at a

cathode current density of 441 amperes/square meter whereupon high purity manganese metal was deposited at the cathode. The current efficiency was 64.8% for a deposition time of 24 hours. Analysis of this metal disclosed only 0.034% S, and negligible traces of cobalt, iron, and nickel.

In the anode compartment, an anolyte was formed having the composition 12.0 grams/liter Mn, 125 grams/liter $(\text{NH}_4)_2\text{SO}_4$, and 29.6 grams/liter of free H_2SO_4 . This anolyte was cooled to approximately 25° C. whereupon complex magnesium salt crystals were formed. These crystals were removed from the solution which was recycled to the leaching step.

EXAMPLE VI

3800 grams of ferromanganese slag (60.7% MnO, 18.96% SiO_2 , 13.92% Al_2O_3 , 0.87% MgO, 0.63% TiO_2 , 0.14% S, 0.08% C, 0.08% Fe, 0.004% Cu, 0.002% Ni, 0.001% Co) was leached with 130 grams of make-up sulphuric acid, and 100 liters of recycled anolyte (containing 12.0 grams/liter Mn, 29.6 grams/liter of free H_2SO_4 , and 125 grams/liter $(\text{NH}_4)_2\text{SO}_4$). This leach slurry was then adjusted to a pH of approximately 6.80 by the addition of ammonia gas. Hydrogen peroxide was added to oxidize the soluble iron. The solution so formed was filtered and 100 liters of filtrate obtained. To this filtrate sulphur dioxide was added to produce cell feed having the composition 27.0 grams/liter Mn, 128 grams/liter $(\text{NH}_4)_2\text{SO}_4$, and 0.50 grams/liter SO_2 .

This cell feed solution was introduced into the cathode compartment of a diaphragm electrolytic cell and electrolyzed at a current density of 462 amperes per square meter. The current efficiency was 60.0% for a deposition time of 24 hours. The manganese metal was found to be of high purity containing only 0.032% S, and traces of Fe, Ni, and Co. The anolyte, after being treated in the manner described hereinabove to remove magnesium, was recycled to the leaching step.

The cyclic process of the present invention may of course be practiced without the magnesium removal steps by directly recycling the anolyte to the leaching step.

In the specific examples given hereinabove to illustrate the steps of the cyclic process, no deficiency of sulphide ions existed in the leach slurry and, hence, the addition of a source of such ions was not required. Moreover, such addition, whenever necessary, is carried out in accordance with procedures that are well known to those versed in the art.

What we claim is:—

1. A process for the production of manganese sulphate or chloride solution substantially free from iron and other heavy metal impurities (e.g., copper, lead, nickel, cobalt, or zinc) which includes leaching an impure manganese-bearing material in sulphuric or

hydrochloric acid to form a leach slurry, adjusting the pH value of the slurry to between 4.0 and 7.5 by the addition of a base in the presence of sufficient sulphide ions to precipitate substantially all of said heavy metal impurities as sulphides, adding an oxidizing agent to precipitate the remainder of the iron impurity, and removing the precipitates from the solution, characterized in that there is used as manganese-bearing material a furnace slag containing manganese in the bivalent state together with a metal sulphide capable of yielding sulphide ions upon reaction with the mineral acid.

2. A process according to Claim 1, in which, when the manganese slag contains less than 0.01% of said heavy metal impurities, the oxidizing agent is added directly to the treated leach liquor containing the sulphide precipitates.

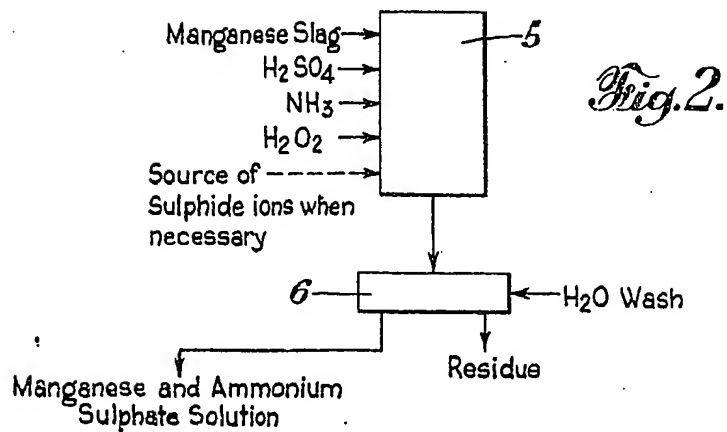
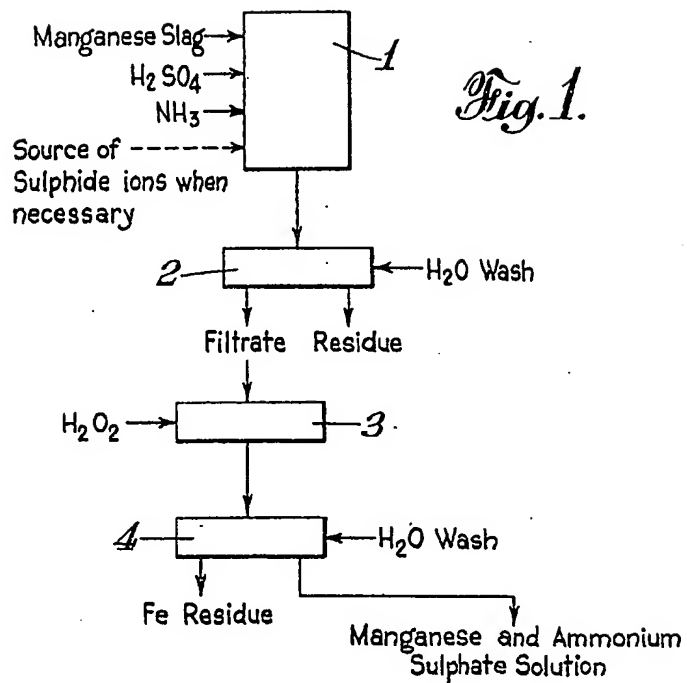
3. A cyclic process for the electrowinning of metallic manganese from a manganese sulphate or chloride solution substantially free from iron and other heavy metal impurities (e.g., copper, lead, nickel, cobalt, or zinc) prepared according to the process claimed in Claim 1 or 2, which comprises adding sulphur dioxide to said solution to form cell feed, introducing said cell feed into the cathode compartment of a diaphragm electrolytic cell, electrolyzing the cell feed to form metallic manganese at the cathode and to form in the anode compartment of said cell an anolyte, and recycling said anolyte to the leaching step.

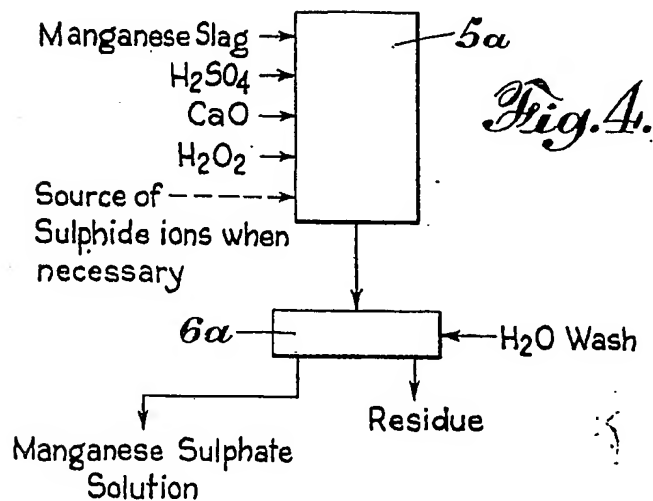
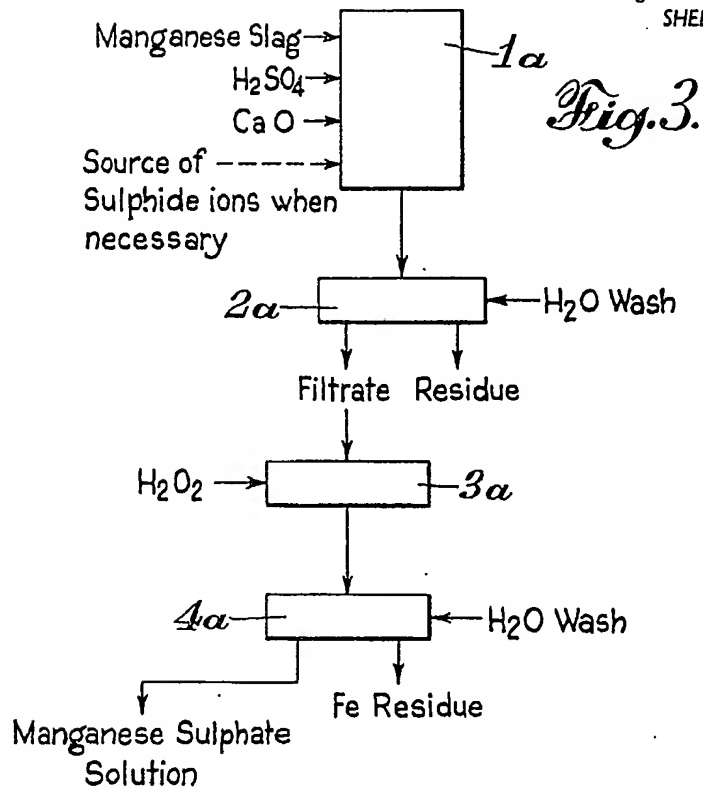
4. A cyclic process as claimed in Claim 3, in which when the manganese-bearing furnace slag contains magnesium, and the leaching agent is sulphuric acid, at least a portion of the anolyte is diverted from recycling to the leaching step and is cooled to a temperature less than the cell operating temperature to form mixed magnesium-manganese-ammonium sulphate crystals and a mother liquor, and that said mother liquor is separated from said crystals and recycled to said leaching step.

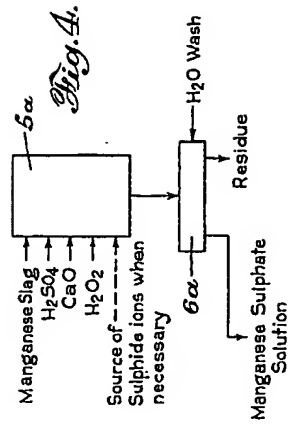
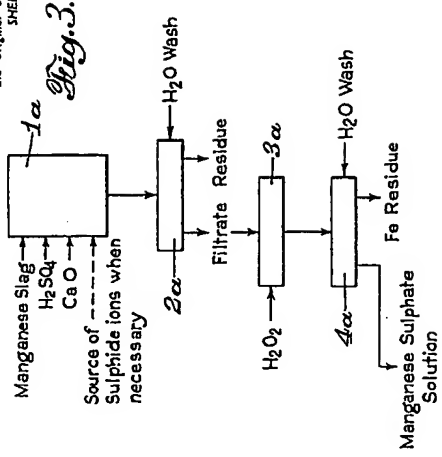
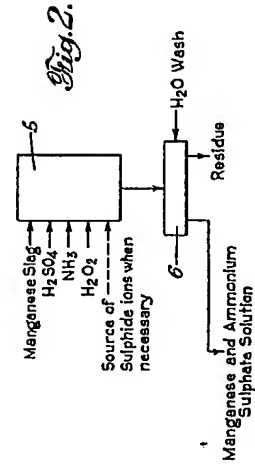
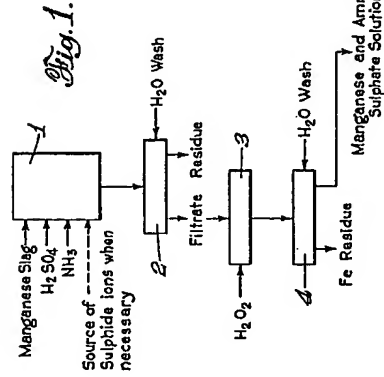
5. A process for the production of manganese sulphate or chloride solution substantially free from iron and other heavy metal impurities (e.g., copper, lead, nickel, cobalt, or zinc), as hereinbefore particularly described and shown in Figs. 1 to 4 of the accompanying drawings.

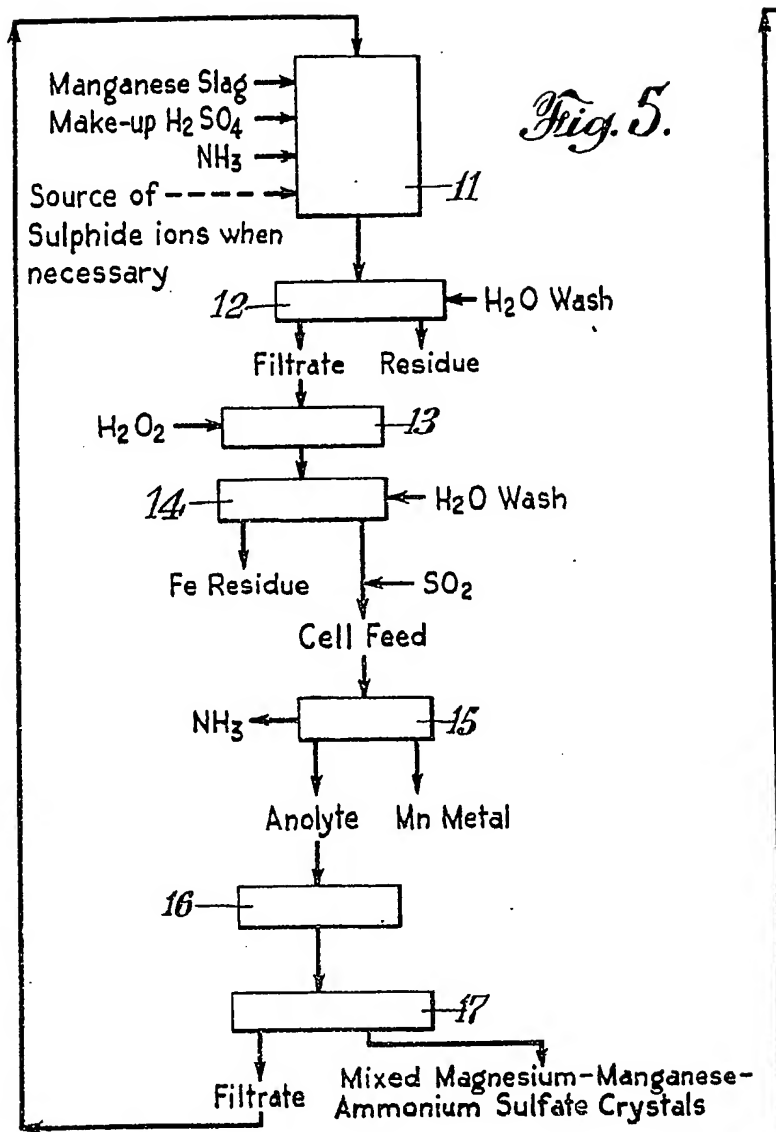
6. A cyclic process for the electrowinning of metallic manganese from a manganese sulphate or chloride solution substantially free from iron and other heavy metal impurities (e.g., copper, lead, nickel, cobalt, or zinc) prepared according to the process claimed in Claim 5, as hereinbefore particularly described and shown in Figs. 5 and 6 of the accompanying drawings.

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COMPLETE SPECIFICATION

3 SHEETS

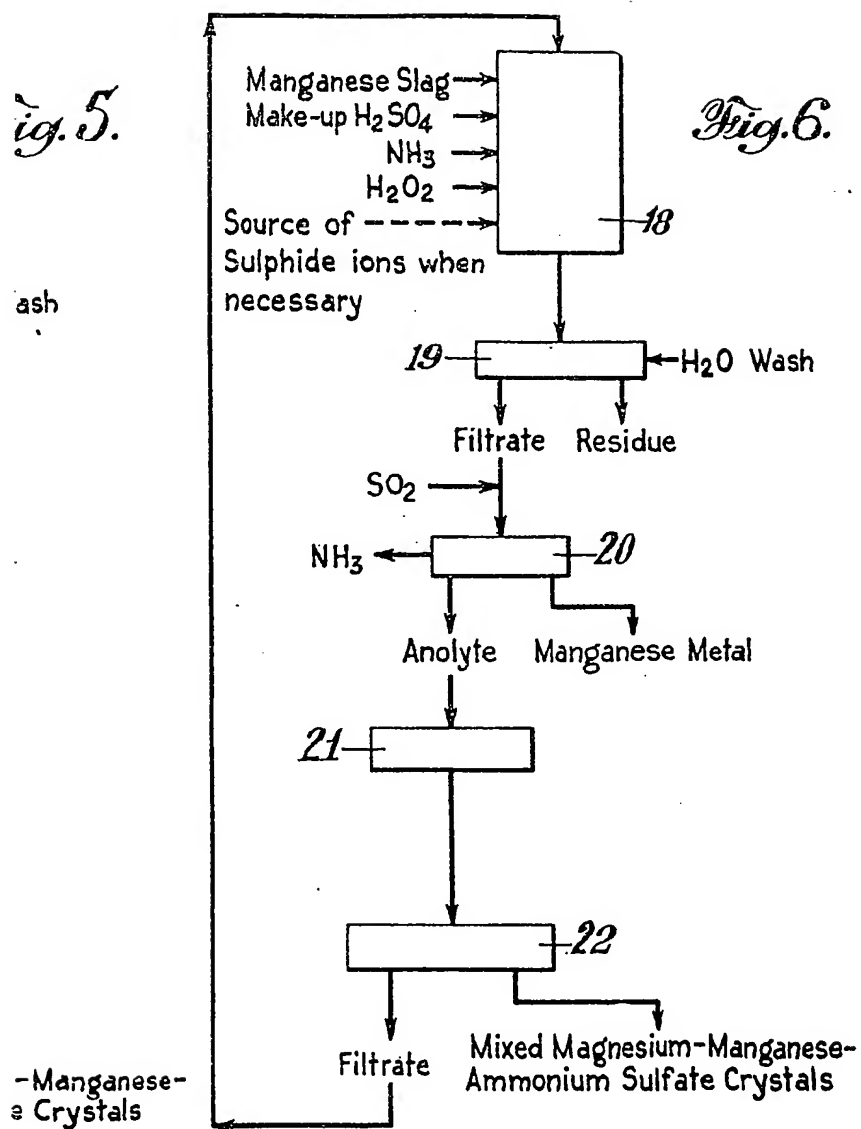
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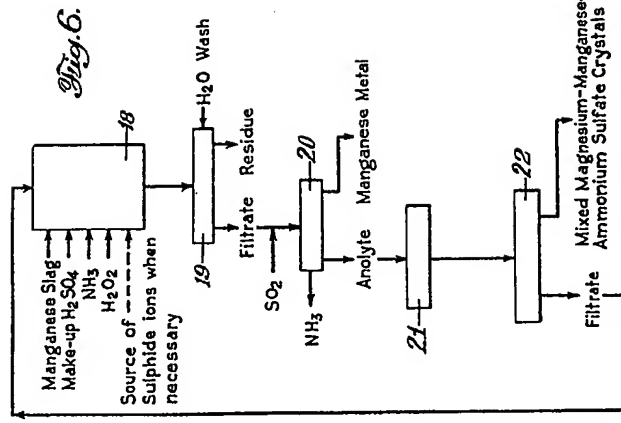
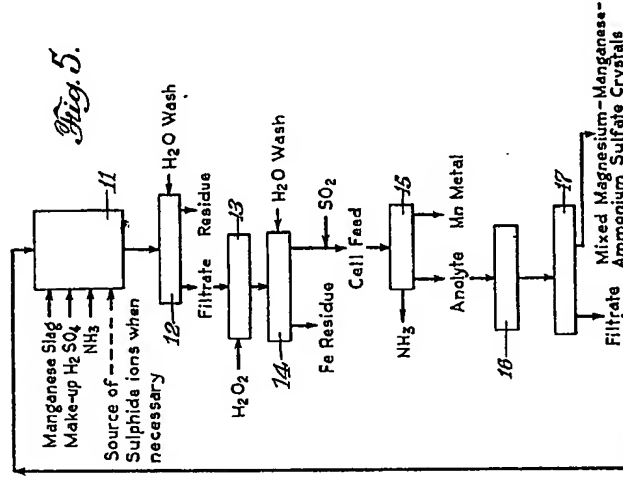
SHEET 3

Fig. 5.

ash

Fig. 6.

-Manganese-
a Crystals



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